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EXPERIMENTAL STUDY OF THE DIFFUSE SCATTERING OF X-RAYS BY POTASSIUM CHLORIDE CRYSTALS

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

1941

By

STANLEY SIEGEL

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Experimental Study of the Diffuse Scattering of X-Rays by Potassium Chloride Crystals

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Diffusely scattered radiation has been studied with a KCl crystal and copper radiation. Observations have been made in the immediate region of a strong reflection. The shapes and half-widths of the maxima have been studied as functions of the direction of incidence. Observations have been found to agree with the theory.

GENERAL

AT the December, 1939, meeting of the American Physical Society in Chicago, W. H. Zachariasen proposed a new theory of the diffuse scattering of x-rays by crystals. In one aspect of the theory, it was predicted that the diffusely scattered x-radiation would appear as sharp diffraction maxima. In a subsequent paper at the same meeting, S. Siegel and W. H. Zachariasen reported an experimental study of these maxima. The results of the theory¹ and experiment² have been published.

The difference between this theory and the earlier work of Debye, as well as the experimental studies by Jauncey and his collaborators, has already been treated.¹

The existence of streaks in Laue photographs has been known for many years, and in 1923, Faxén³ suggested that these streaks might be caused by a thermal effect in the crystal. Wadlund⁴ observed very prominent streaks in some photographs and Zachariasen⁵ interpreted these as being due to a two-dimensional lattice effect. Recently Preston⁶ has shown the effect of temperature on these streaks, thus confirming Faxén's suggestion. Preston observed streaks when general radiation was used; however, when monochromatic radiation was used, maxima, similar to Laue spots, appeared. Preston interpreted these on the basis that the thermal vibrations of the lattice break the crystal into groups composed of an atom and its nearest neighbors,

and these thermal motions change the interatomic distance from one group to another, thus producing new maxima. Raman, apparently unaware of Preston's work, or of the work carried out at Ryerson Laboratory, published photographs showing these spurious maxima.⁷ He interpreted the maxima as a specular reflection of x-rays resulting from stratifications of density in the crystal which are not static but dynamic in character. Other articles have since appeared. Knaggs and collaborators⁸ have published photographs of these maxima. Lonsdale and collaborators⁹ have made a detailed qualitative study of this effect. The conclusions reached by them are those predicted by theory, many of the results however, having been already studied quantitatively. More recently, another paper by Raman and Nilakantan has appeared.¹⁰

Although the agreement between theory and observations in our original experiment was quite good, there was some discrepancy between theoretical and observed widths of the diffuse maxima. Thus it was decided to carry out the observations in more detail, to extend them as close as possible to the Bragg angle, and to increase the accuracy of observations with better equipment. The original experiment was performed with a crystal of sodium chloride. Since the theory was developed for crystals containing atoms of only one kind, a good approximation to such a case would be potassium chloride, which was used throughout the present experiment.

¹ W. H. Zachariasen, *Phys. Rev.* **57**, 597 (1940).

² S. Siegel and W. H. Zachariasen, *Phys. Rev.* **57**, 795 (1940).

³ H. Faxén, *Zeits. f. Physik* **17**, 266 (1923).

⁴ A. P. R. Wadlund, *Phys. Rev.* **53**, 843 (1938).

⁵ W. H. Zachariasen, *Phys. Rev.* **53**, 844 (1938).

⁶ G. D. Preston, *Proc. Roy. Soc.* **172**, 116 (1939).

⁷ C. V. Raman and P. Nilakantan, *Nature* **145**, 667 (1940); *Proc. Ind. Acad. Sci.* **11**, 379 (1940).

⁸ I. E. Knaggs, K. Lonsdale, A. Müller, A. R. Ubbelohde, *Nature* **145**, 820 (1940).

⁹ K. Lonsdale, I. E. Knaggs, H. Smith, *Nature* **146**, 332 (1940).

¹⁰ C. V. Raman and P. Nilakantan, *Proc. Ind. Acad. Sci.* **12**, 141 (1940).

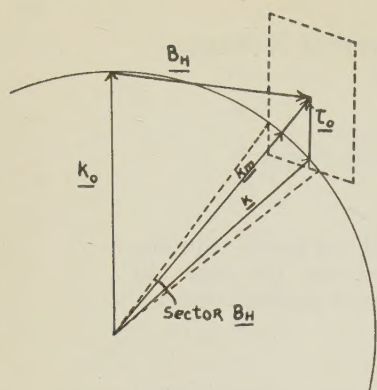


FIG. 1. A section of the reciprocal lattice.

METHODS FOR OBSERVING THE MAXIMA

As the theory indicates, the streaks are produced by the continuous radiation in the x-ray beam while the spots are individual diffraction maxima due to the characteristic radiation. In the present paper only the diffuse spots will be dealt with. These maxima are observed whenever Bragg's law is nearly satisfied.

Figure 1 shows the conditions under which they may be observed. This figure and the following description have been given in Zachariasen's paper.¹ Vectors $\mathbf{k}_0$ and $\mathbf{k}$ are the directions of incidence and scattering of the x-ray beam. $|\mathbf{k}_0| = |\mathbf{k}| = 1/\lambda$. $\mathbf{B}_H$ is a vector in the reciprocal lattice, and its shortest separation from the vector $\mathbf{k} - \mathbf{k}_0$ is τ_0 . Let $\mathbf{k}$ vary. Its terminus will describe a sphere of radius $1/\lambda$ about the terminus of $-\mathbf{k}_0$, thus producing the sphere of reflection. The points on the sphere of reflection which are closer to $\mathbf{B}_H$ than to any other lattice point define a sector of the solid angle 4π , so that the same vector $\mathbf{B}_H$ is associated with all directions $\mathbf{k}$ within the sector. As $\mathbf{k}$ varies within a sector, τ_0 varies with it since $\mathbf{k} - \mathbf{k}_0 + \tau_0 = \mathbf{B}_H$. Considering $\mathbf{k}_0$ and $\mathbf{B}_H$ to be fixed, τ_0 becomes a minimum value, $\tau_{\min}$ when $\mathbf{k}$ is parallel to $\mathbf{B}_H + \mathbf{k}_0$. Thus $\tau_{\min} = |\mathbf{B}_H + \mathbf{k}_0| - |\mathbf{k}|$ or $\lambda\tau_{\min} \approx -\Delta \sin 2\theta_B$, where θ_B is the Bragg angle and $\theta_i \equiv \theta_B + \Delta$, Δ being a small deviation from the Bragg angle. The intensity of the scattering reaches a maximum whenever τ_0 is a minimum, and the direction of the intensity maximum, $\mathbf{k}_m$, is $[1 + \lambda\tau_{\min}]\mathbf{k}_m = \mathbf{B}_H + \mathbf{k}_0$. The scattering angle corresponding to the maximum is shown to be $2\theta_m \approx 2\theta_B + 2\Delta \sin^2 \theta_B$. For scattering directions $\mathbf{k}$ near a maximum $\mathbf{k}_m$, $(\lambda\tau_0)^2 = (\lambda\tau_{\min})^2 + \chi^2$ where χ

is the angle between $\mathbf{k}$ and $\mathbf{k}_m$. The intensity distribution is symmetrical about the maximum, and the half-width at half-maximum is $\chi_{\frac{1}{2}} \approx \lambda|\tau_{\min}| = |\Delta| \sin 2\theta_B$.

Thus, in a transmission photograph there will always be some reflection planes for which $\tau_{\min}$ will give appreciable intensity, enough to be conveniently recorded.

Transmission photographs were obtained by Preston and later by Raman. They obtained Laue photographs using apparently large pinholes to define the primary beam, and employing sensitizing screens to hasten recording. But for quantitative work it is necessary to use a narrow pinhole or slit to keep the divergence of the beam at a minimum and to avoid the use of sensitizing screens, for such screens widen the spots, causing them to become too diffuse for any width or intensity measurements. The author tried to obtain transmission photographs using a small pinhole, monochromatic copper radiation, and a thin KCl crystal. One would expect weak reflections with Cu $K\alpha$ and KCl, except at a scattering angle of 90° , in which case the absorption would become quite large. After a 36-hour exposure only very faint spots were discernible. The transmission method does not appear very amenable to a quantitative study.

The best method for observation is obtained by reflecting the primary beam from the crystal surface and making observations on a strong reflection. In this case the crystal can be set to produce any desired $\tau_{\min}$ values, and, depending on the nature of the crystal surface, observations can be made on diffuse maxima having relatively large intensity values. It must be remembered, however, that in any method of observation, the divergence of the primary beam must be smaller than the widths of any of the observed diffuse maxima. This immediately rules out the use of wide slits or sensitizing screens, and gives rise to small recording intensities. This point will be elaborated.

APPARATUS AND EXPERIMENT

A Bragg spectrometer was used in making observations. All such observations could be duplicated to within $1'$ of arc, so that any error was less than that value. The beam was defined

by two slits separated a distance of 8.0 cm. The width of each slit was 0.005 cm, the height being 0.3 cm. The distance between the second slit and crystal was 5.0 cm, and between crystal and photographic plate, 6.04 cm. A copper x-ray tube was used throughout the experiment and the radiation was filtered with a nickel foil. Special care was taken in orienting the crystal so that the same facial area would always receive the same illumination. This was accomplished by the usual optical methods. The photographic plate was mounted normal to the incident beam.

Before observations of any kind are made, it is of primary importance to have as "perfect" a crystal surface as possible. The theory calls for a well-defined beam. The divergence of the beam reflected from the crystal face must, of course, be narrower than the widths of any of the recorded maxima. The maxima are sharpest at the Bragg angle and become broad and diffuse as the crystal is rotated from its Bragg position. Hence the narrowest maximum is determined by the point of observation closest to the Bragg angle for the characteristic radiation producing the maximum. Observations cannot be made at the Bragg angle, for the diffuse temperature maximum and the Bragg reflection coincide. Thus the crystal is slightly rotated away from its Bragg angle so that the Bragg reflection is completely suppressed and will not interfere with the emitted temperature maximum. It is found however, that most crystal surfaces are rough and warped, and this allows the Bragg reflection to persist over quite an angular range about the Bragg angle.

Experimental difficulties have been encountered at this point. In the original experiment with NaCl it was found that the Cu $K\alpha$ line reflected from the (200) face could persist even though the crystal was rotated $60'$ from its Bragg position. The diffuse maxima cannot be studied under such conditions for they are very nearly superimposed upon the persistent Cu $K\alpha$ line, and it was only by properly etching the surface that the line radiation disappeared when the crystal was $30'$ from the Bragg position. If the intensity of the line radiation is plotted as a function of the deviation of the crystal away from the Bragg position for the line, then one obtains a "surface distribution curve." Etching the surface produces "surface distribution curves"

of various shapes and widths. Large primary slits allow illumination of a larger facial area, and this increases the persistence of the Bragg reflection.

Therefore, if observations are to be made on the sharp intense temperature maxima near the Bragg angle, a good crystal surface showing a rapid cut-off of the Bragg reflection must be used. Such a surface will exhibit a narrow distribution curve. After determining the point of observation closest to the Bragg angle, slit widths can be approximately adjusted to account for the narrowest diffuse maximum which will be emitted at that point.

In the present experiment an extraordinary KCl crystal section was cleaved from its parent. The parent was an artificial crystal. The cleavage (200) surface was so perfect that the Bragg angles for each component of the Cu $K\alpha$ doublet were quite sharply determined. Figure 2 shows the appearance of the doublet on rotation of the crystal through the Bragg angles for the doublet. In Fig. 2(a) $K\alpha_1$ is strongly reflected while $K\alpha_2$ is barely visible. In Fig. 2(b) $K\alpha_2$ has increased in intensity so that its intensity is greater than that of $K\alpha_1$. Figure 2(c) shows that $K\alpha_1$ has still decreased in intensity. The angles indicated in the figure are arbitrary. A surface distribution curve for this crystal has been made. Two curves are possible, one for each component of the doublet. The deviation of the crystal away from the average Bragg angle for the doublet is indicated by Δ . For $\Delta = 6'$ the intensity of the

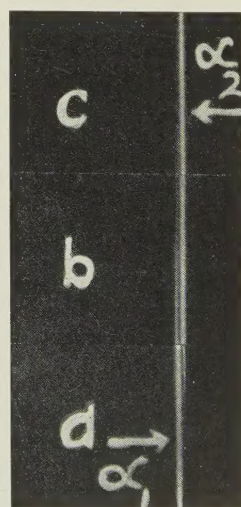


FIG. 2. Showing the change in intensity of each component of the Cu $K\alpha$ doublet over a three-minute interval in the crystal angle. These lines are magnified. The lines tend to break up when the crystal is moved too far from the Bragg positions.

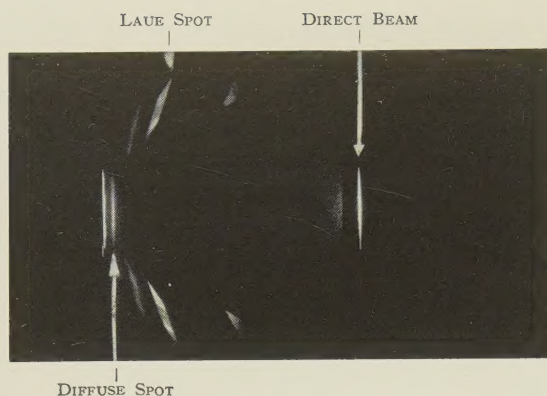


FIG. 3. Typical photograph for $\Delta=29'$. The exposure time is 32 hours. The diffuseness of the temperature maximum can be seen extending into the Laue spot. A diffuse temperature halo can be seen surrounding the direct beam.

emitted doublet became weak enough to make observations on the temperature maximum. A 5-hour exposure on the photographic plate yielded a temperature maximum and only a very faint doublet which did not interfere.

The necessity for such a narrow beam made the use of the ionization-chamber method impossible for recording the intensities of the diffuse maxima. For studying the widths of the lines, the analyzing slit in front of the ionization chamber must measure the differential intensity and must thus be narrower than the primary slits. Even then the intensity of a diffuse line for $\Delta=40'$ say, may be about 10^{-4} that of the Cu $K\alpha$ line emitted at the Bragg angle.

In making observations, the crystal was oriented so that the cleavage face would reflect at the average Bragg angle for the Cu $K\alpha$ doublet. All diffuse maxima were then due to the line radiation. The intensity of the continuous radiation is small in comparison with that of the Cu $K\alpha$ lines, so that the diffuse scattering of the continuous radiation can be neglected. Since the crystal was quite perfect, observations began for $\Delta=6'$ and extended up to $\Delta=41'$. For $\Delta=6'$ the exposure time to produce the maximum was 5 hours, and for $\Delta=41'$ the exposure time was 71 hours. The exposure time varies approximately as $1/\Delta^2$. Thus any observations beyond $\Delta=41'$ would require extremely long exposures.

EFFECT OF TEMPERATURE

All observations in this experiment were made at room temperature. However, the diffuse

maxima have been studied over a wide range of temperatures. Lonsdale and workers have observed them at liquid-air temperatures. They find the diffuse spot pattern disappears almost completely at that temperature. Raman and Nilakantan have observed them from room temperature up to 275°C and find an increase in intensity at higher temperatures. Preston has made observations at 500°C and finds increased intensity. The observations include a variety of crystals.

EXPERIMENTAL RESULTS

Figure 3 shows a typical photograph. For this case $\Delta=29'$ and the exposure time is 32 hours. The diffuseness of the temperature maximum may not be apparent from the reproduction given, but a photometer tracing reveals that it extends well into the Laue spot next to it. The geometrical patterns are the Laue reflections. The Laue reflection next to the diffuse line is very uniform and regular, indicating the quality of the crystal face.

According to theory, the direction of scattering corresponding to an intensity maximum of the diffuse radiation lies in the plane of incidence, and the scattering angle is $2\theta_m = 2\theta_B + 2\Delta \sin^2 \theta_B$.

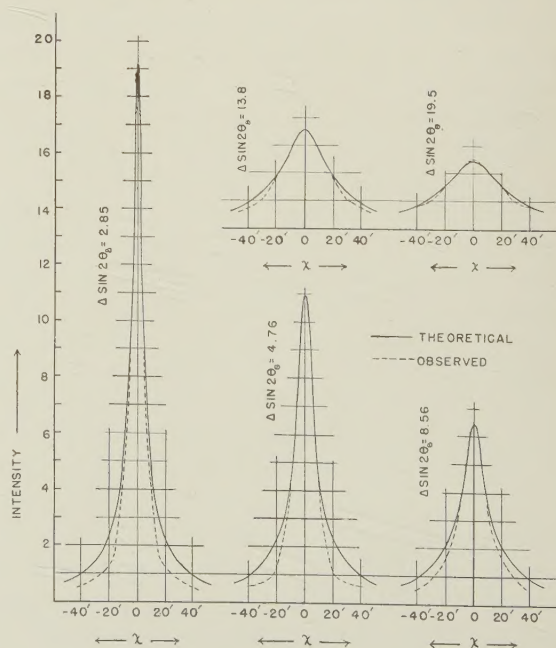


FIG. 4. Shape of the diffraction maxima for different values of $|\Delta|$.

If the incident beam is a narrow pencil, the intensity near a maximum is

$$J_2 = \frac{K}{(\Delta \sin 2\theta_B)^2 + \chi^2 + \varphi^2},$$

where χ and φ are the angular deviations from the maximum in the plane of incidence and normal to it. If Δ , χ , and φ remain small, K can be treated as a constant. However, in this experiment a slit was used. The intensity measurements were made in the plane of incidence, so that the above equation must be integrated with respect to φ . The result is

$$J_2 \propto \tan^{-1}(\varphi_m/y)/y, \quad y = [(\Delta \sin 2\theta_B)^2 + \chi^2]^{\frac{1}{2}},$$

where $\varphi_m = l/2R$ and l is the height of the slit. R is the distance from the crystal to the point of observation. In the present experiment φ_m was $85.2'$.

Figure 4 shows the shape of the diffuse temperature maxima for various values of $\Delta \sin 2\theta_B$, θ_B being the average Bragg angle for $\text{Cu } K\alpha_{1,2}$. The experimental curves were calculated from photometer tracings of the plates. The agreement between observed and theoretical shapes of the maxima is quite good.

In Fig. 5 $\chi_{1/2}$ represents the half-widths at half-maximum. $\chi_{1/2}$ is plotted as a function of $\Delta \sin 2\theta_B$. The circles represent single measurements. In some cases it was necessary to average the values obtained from more than one tracing. These latter points are indicated by crosses. According to theory the maxima do not appear at an angle $2\theta_B$ but at an angle $2\theta_B + 2\Delta \sin^2 \theta_B$. This means the lines are shifted by a matter of some seconds. This has been observed on some of the plates, but it is too small to measure accurately. It will change the experimental half-widths by a very small amount only.

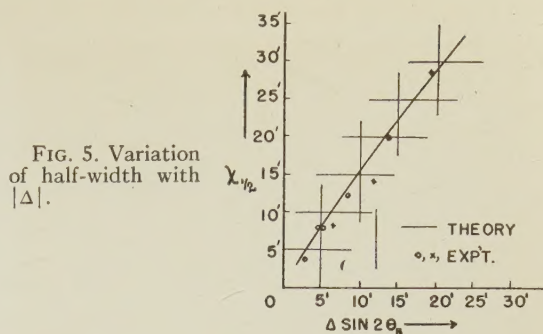


FIG. 5. Variation of half-width with $|\Delta|$.

SUMMARY

All measurements have been made on maxima due to the line radiation present in the incident beam, and only a simple crystal, KCl , has been studied. The crystal has been found to exhibit a perfect surface for this study. The observations extend from $\Delta = \pm 6'$ to $\Delta = \pm 41'$. The shapes and widths of the maxima have been found to agree quite well with the theory.

A study of the variation of the peak intensities of the maxima with $\Delta \sin 2\theta_B$ has previously been made.² This variation of intensity is the background present about each reflection in an oscillation photograph. For every Laue reflection there is associated with it a diffuse temperature maximum. However, maxima may arise in directions other than those of the Laue directions in the manner indicated. The intensity of the maxima has been shown to increase with increased rise in temperature. The theory indicates that there should be a slight increase in intensity of the diffuse radiation in a region about the zero angle of scattering. Figure 3 shows that it is manifest as a halo about the transmitted direct beam.

The author wishes to thank Dr. Zachariasen for suggesting the problem and for his valuable aid and criticism during the investigation.



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